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Silicic acid: The omniscient molecule

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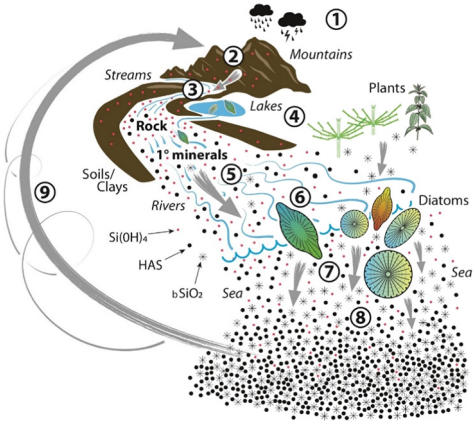
HIGHLIGHTS

- Silicic acid plays a fundamental role in planetary health.
- Silicic acid is a small neutral molecule.
- Silicic acid keeps aluminium out of biota.
- Silicic acid is deposited as biogenic silica.
- The silicic acid cycle is Earth's thermostat and contributes towards climate change.

GRAPHICAL ABSTRACT

The Silicic Acid Cycle is Earth's Thermostat.



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ABSTRACT

We contend that silicic acid is a much under-valued molecule and specifically in the context of its role in establishing and maintaining life on Earth. Silicic acid can also be an ill-understood molecule with its chemistry all too often confused with that of either silicates or silica. Herein we (i) provide a working definition for silicic acid; (ii) identify its omnipresent role in biochemical evolution in excluding aluminium from biota and providing adventitious benefits through biological silicification and (iii) explain how the silicic acid cycle is intrinsic to climate change.

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1. What is silicic acid?

The Earth's crust is formed primarily of three elements, oxygen, silicon, and aluminium, arranged as aluminosilicate minerals. Paradoxically, only one of these, oxygen, is considered as essential to life. The Earth's crust is in a continuous cycle of dissolution and reformation

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over geological time (Exley, 1998, 2003). Rainfall induces the non-congruent dissolution of these minerals with silicon released ahead of aluminium (Bennett et al., 1988; Brady and Walther, 1989). Silicon dissociates from the minerals of the Earth's crust as silicic acid, a silicon atom surrounded by four hydroxyl groups in a tetrahedral configuration (Exley and Sjöberg, 2014). The silicic acid molecule can be thought of as a non-uniform corpuscular-like body with a maximum radius of approximately four Ångströms (Fig. 1). Silicic acid is soluble up to an approximate concentration of 2 mmol/L. Above this concentration it auto-condenses to eventually precipitate as silica. Silicic acid is a very weak acid (pka ~9.5), essentially an acid by name only, and loses its first proton as the solution pH approaches 10. There are few natural environments on the Earth's surface where solution pH are above 10. The consequence of high solubility and low acidity is that following its dissolution from minerals of the Earth's crust silicic acid exists, in the main, as an uncharged monomer and it is in this form (Fig. 1) that it enters biogeochemical cycles (Exley, 1998, 2003).

2. Silicic acid reacts with itself to form silica

Silicic acid exists in equilibrium with monosilicate anions though it is primarily undissociated until solution pH exceed its pK_a of approximately 9.5 (Eq. (1)).

$$Si(OH)_4 \leftrightarrow SiO(OH)_3^- + H^+ \quad pK_a = 9.472 \tag{1}$$

$$Si(OH)_4 + M^{X+} \leftarrow SiO(OH)_3M \quad M = \text{Any di or trivalent metal} \tag{2}$$

In under-saturated solutions of silicic acid there is evidence, neither at the bench nor in silico, of any stable chemistry between monosilicate anions in equilibrium with silicic acid and any other moiety, inorganic or organic. For example, there is no experimental evidence that any metal cation affects the equilibrium between silicic acid and monosilicate in an under-saturated solution of the former (Eq. (2)). Silicic acid, as is released to the geosphere, pedosphere, and hence, biosphere, is essentially inert at least until it reaches saturation (*ca* 2 mmol/L) at which point it may precipitate as amorphous silica (Exley and Sjöberg, 2014) (Eq. (3)).

$$\begin{gathered} 2Si(OH)_4 \leftrightarrow (HO)_3SiOSi(OH)_3 + H_2O \\ n\left[(HO)_3SiOSi(OH)_3\right] + n\left[Si(OH)_4\right] \leftrightarrow \left[SiO_{n/2}(OH)_{4-n}\right]_m \quad K_{sp} = 2 \text{ mmol/L} \end{gathered} \tag{3}$$

Situations where concentrations of silicic acid in the natural environment approach or even exceed the solubility of amorphous silica, while uncommon today, would have been more commonplace on early Earth (Cloud, 1965). Since silicic acid in an under-saturated solution has neither inorganic (with one exception discussed below) nor organic chemistry, it simply equilibrates according to its least soluble salt which, in the natural environment, is amorphous silica (Siever, 1992). It was the arrival of the biosphere and subsequently the advent of biological silicification, the catalytic formation and deposition of silica that had the largest impact upon the chemistry of silicic acid on Earth (Exley, 1998).

3. Silicic acid reacts with aluminium

This description of silicic acid as a largely benign participant in the geochemistry of early Earth is actually highly misleading as it omits silicic acid's unique inorganic chemistry with aluminium (Birchall et al., 1989), the only known exception to the rule highlighted previously herein. While silicic acid has no relevant chemistry with any metal cation, including that of aluminium, Al^{3+}, it does undergo a competitive (with hydroxyaluminium) substitution across adjacent hydroxyl groups on a template of aluminium hydroxide to form hydroxyaluminosilicates (Beardmore et al., 2016; Exley, 2012) (Fig. 1). This unique inorganic chemistry forms an integral part of the biogeochemical cycles of both silicon and aluminium (Exley, 1998, 2003). The incongruent dissolution of rock by the combined action of wet and dry deposition results in the release of silicic acid and the subsequent formation of an aluminium-rich surface layer. While the solubility of the resultant aluminium 'ore',

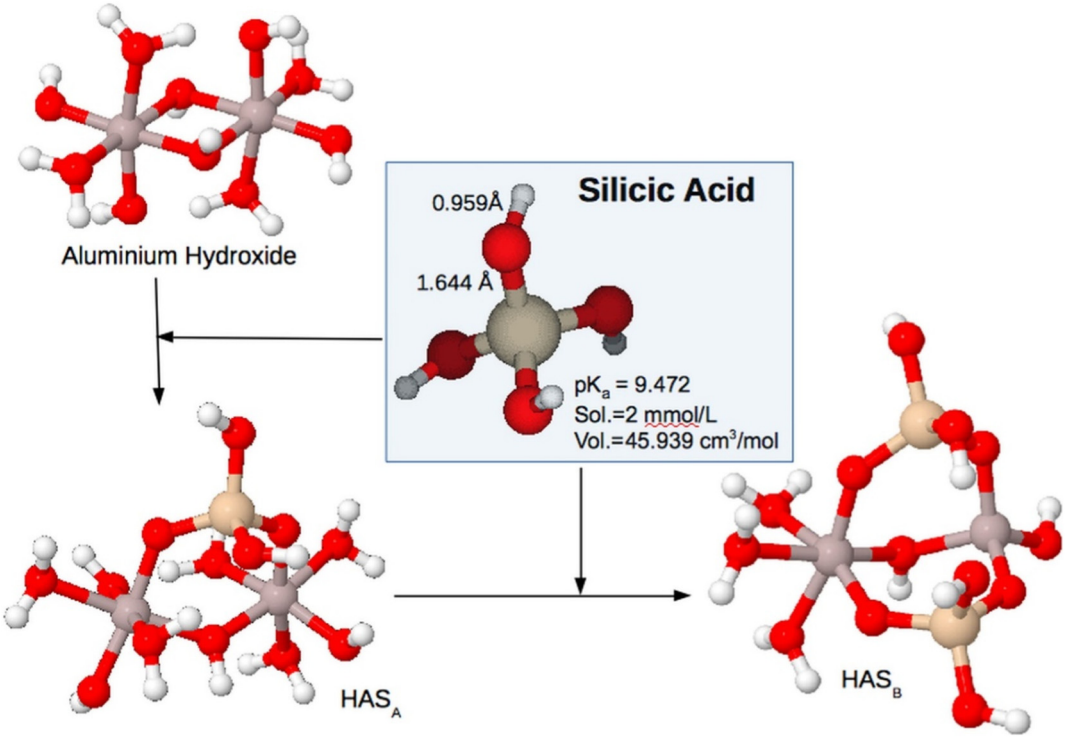

Fig. 1. The formation of hydroxyaluminosilicates, HASA and HASB, from the reaction of aluminium hydroxide and silicic acid (HASA) and HASA and silicic acid (HASB). Structures are optimisations using Density Functional Theory[10].

for example bauxite, is relatively low, it will exhibit surface dissolution and undergo the release of its free metal cation, $Al^{3+}{}_{(aq)}$. Where the pH of incipient rainfall is determined by carbonic acid equilibria, approximately pH 6 (Eq. (4)), the solubility of $Al^{3+}{}_{(aq)}$ in soil waters may be low and its immediate precipitation as a sparingly soluble amorphous aluminium hydroxide will follow (Burrows and Hem, 1977) (Eq. (5)).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad pK_a = 6.1 \tag{4}$$

$$Al^{3+}{}_{(aq)} \leftrightarrow AlOH^{2+}{}_{(aq)} \leftrightarrow Al(OH)_2{}^{+}{}_{(aq)} \leftrightarrow Al(OH)_{3(s)} \leftrightarrow Al(OH)_4{}^{-}{}_{(aq)} \tag{5}$$

However, the formation of sparingly soluble aluminium hydroxide ($Al(OH)_{3(s)amorphous}$) in the presence of silicic acid instantaneously results in significantly less soluble hydroxyaluminosilicate solids ($HAS_{(s)}$) (Beardmore et al., 2016). Silicon as silicic acid acts as a geochemical control over the growth and precipitation of aluminium hydroxide in natural environments, such as soil solution and surface waters (Pačes, 1978). While silicic acid's role in the formation of hydroxyaluminosilicates does not impact significantly upon its environmental abundance, it is essential in limiting the concentration of $Al^{3+}{}_{(aq)}$ in soil, ground and surface waters and in delivering aluminium in an inert form back, via the sedimentary cycle, to its origin in the Earth's crust (Exley, 2003) (Fig. 2). The evolution of life on Earth was coincident with the geochemical cycles of aluminium and silicon (Exley, 1998, 2003, 2009a). Neither of these elements played an active role in biochemical evolution since silicon, though abundant as silicic acid, was biochemically inert, while aluminium as Al^{3+}, though chemically reactive, was biologically unavailable through the formation of hydroxyaluminosilicates (Exley, 2009a). The first (and continuing) major role of silicic acid was in acting as a significant pressure upon the natural selection of the elements in the evolution of biochemical processes. Specifically, the absence of biologically available aluminium supported essential roles for metals such as magnesium, calcium, and iron in biochemistry. In the absence of an abundance of silicic acid, biologically reactive aluminium would have been an active participant in early biochemical evolution (Exley, 2009a). We cannot know how this would have affected life on Earth, as we know it today.

4. Silicic acid and mineral weathering

Silicic acid plays a primary role in mineral weathering (Berner et al., 1983). As the significant soluble product of carbon dioxide driven dissolution of aluminosilicate rocks, silicic acid influences the kinetics or rate of weathering (Berner et al., 1983). Through equilibrium dynamics, the

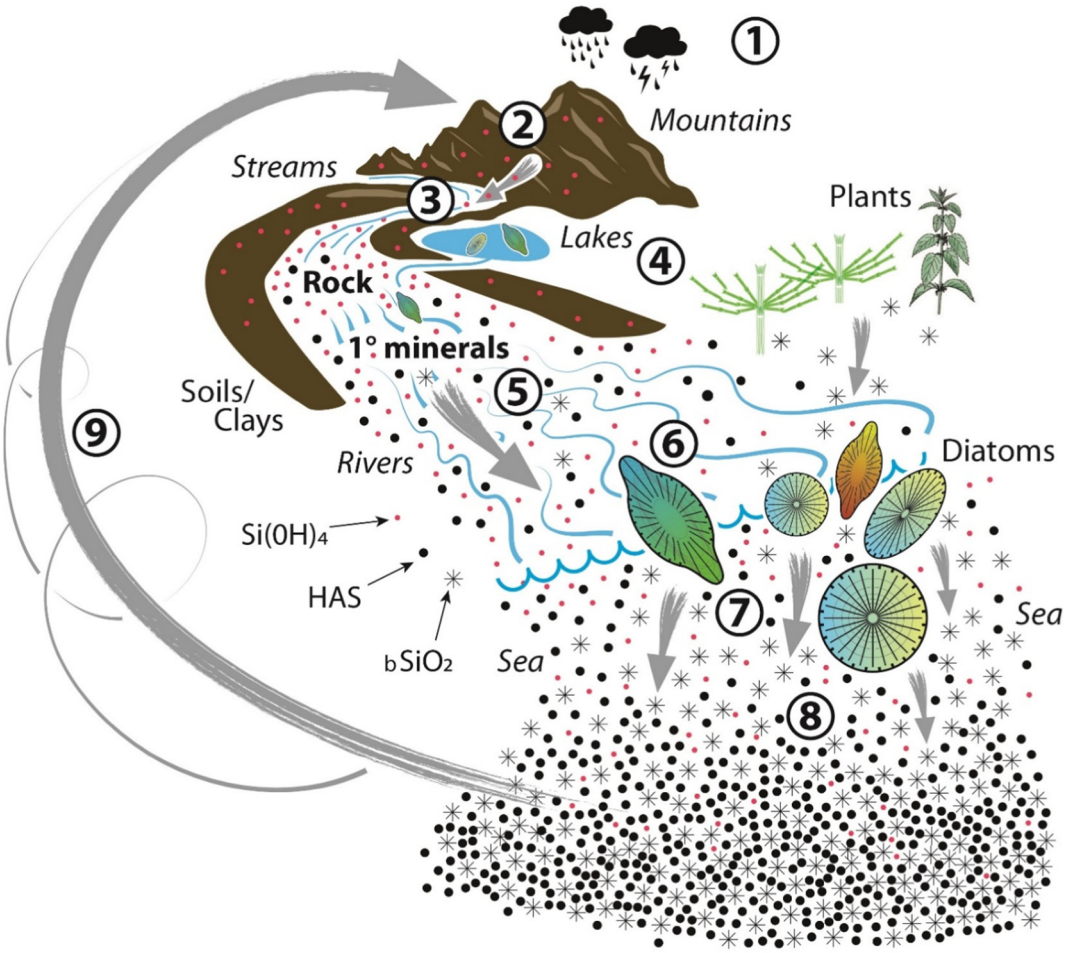

Fig. 2. The silicon cycle. 1. Rainfall dissolves mountains over millions of years. 2. Incongruent dissolution of the Earth's crust releases silicon as silicic acid, $Si(OH)_4$. 3. Dissolution products including primary minerals, clays, soil and silicic acid enter soil waters, streams, lakes and rivers. 4. Terrestrial plants such as horsetail capture silicic acid and deposit it in their tissues as biogenic silica ($bSiO_2$). 5. Silicic acid reacts with aluminium to form hydroxyaluminosilicates (HAS). 6. Diatoms in freshwaters harvest silicic acid and deposit it as biogenic silica in their frustules. 7. In the sea, diatoms are the major sink for silicic acid. 8. Biogenic silica, primarily from dead diatoms, and HAS, mainly from the edaphic environment, sink slowly and enter the sedimentary cycle. 9. Silicon is recycled as constituents of the Earth's crust over millions of years.

concentration of silicic acid in any given environment is potentially a brake on mineral weathering. The advent of biological silicification and primarily by diatoms had the effect of lowering the concentration of silicic acid in the natural environment and releasing this brake. Biological silicification is a mechanism by which silicic acid harvested from environments in which it is significantly under-saturated is concentrated and subsequently deposited as amorphous biogenic silica (Exley, 2009b). Biological silicification, through the removal of silicic acid from solution, acted as an accelerant of carbon dioxide fuelled mineral weathering and in consequence lowered atmospheric levels of carbon dioxide and contributed significantly to global cooling (Berner et al., 1983). The biological availability of silicon as silicic acid is acting as a cooling system for Earth so why is contemporary Earth warming.

An often-overlooked consequence of the burning of fossil fuels is a shift in the major acidifying anion in both wet and dry deposition. In many regions of the planet, the pH of rainfall is no longer governed by carbonic acid, but by much stronger mineral acids and primarily sulphates. In these regions, there has been a switch in the major acidifying anion in rainwater brought about by release of sulphur and nitrous oxides in anthropogenic emissions (Amiotte Suchet et al., 1995). The consequences for mineral weathering and silicic acid as a global coolant are primarily two-fold. The first is that sulphuric and not carbonic acid is the primary reactant in aluminosilicate weathering (Paces, 1986). Consequently, less atmospheric carbon dioxide is drawn down directly through mineral weathering (Amiotte Suchet et al., 1995). The second is that the products of mineral weathering, where sulphate is the major anion, are different to those where bicarbonate is dominant (Eqs. (6) & (7)) (Wollast and Mackenzie, 1983). This shift in pattern of mineral weathering is sometimes evident in regions heavily impacted by acid deposition as changes in clay mineral profiles (Rampazzo and Blum, 1992). A further possible consequence of such a change in acid-fuelled mineral weathering is a two-fold reduction in the stoichiometric release of silicic acid (see Eqs. (6) & (7)) (Wollast and Mackenzie, 1983).

The weathering of potassium feldspar where carbonic acid is the principal weathering acid in rainfall, a relatively slow reaction rate; $10^{-15.5}$ μmol m^{-2} s^{-1}

$$\underset{\text{K-Feldspar}}{2KAlSi_3O_8} + 2CO_2 + 11H_2O \rightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 2K^+ + 2HCO_3^- + \underset{\text{Silicic Acid}}{4Si(OH)_4} \quad (6)$$

The weathering of potassium feldspar where sulphuric acid is the principal weathering acid in rainfall, a relatively fast reaction rate; $10^{-14.6}$ μmol m^{-2} s^{-1}

$$\underset{\text{K-Feldspar}}{2KAlSi_3O_8} + H_2SO_4 + 4H_2O \rightarrow \underset{\text{Montmorillonite}}{Al_2Si_4O_{10}(OH)_2} + 2K^+ + SO_4^{2-} + \underset{\text{Silicic Acid}}{2Si(OH)_4} \quad (7)$$

Carbon dioxide fueled aluminosilicate mineral dissolution acts as a slow-release system for silicic acid, while sulphuric acid fueled dissolution is more rapid, but less productive per mole of aluminosilicate mineral (Wollast and Mackenzie, 1983). It has been argued that the industrial revolution and the concomitant acidification of the atmosphere primarily through burning fossil fuels resulted in an accelerated diminution of biologically available silicic acid (Exley, 1998). One possible consequence of such would be a fall in primary productivity, predominantly attributable to diatom populations in the oceans, and a concomitant reduction in the drawdown of carbon dioxide from the atmosphere. Is this one of the reasons why the Earth is warming?

5. Biological silicification and climate change

We have described the silicic acid cycle (Fig. 2) as Earth's thermostat. While its role as either an agent of cooling or warming is influenced by the formation of hydroxyaluminosilicates (and so keeping aluminium out of biota), it is the balance between its formation (the dissolution of mountains) and its biologically catalysed precipitation as biogenic silica (biological silicification) that determines which of these pathways (cooling or warming) will predominate. Understanding of the detailed mechanism of biological silicification in plants and diatoms remains equivocal. It is a subject fraught with confusion largely emanating from a refusal among participating scientists to accept that the bioinorganic chemistry of biological silicification is that of silicic acid and not silicates or other ill-defined forms of silicon (Exley, 2015). Cell biochemistry is a true catalyst of biological silicification in that while enabling it, the biochemical machinery at its heart remains unaltered upon the deposition of biogenic silica (Guerriero et al., 2018b). The challenge has been to describe biological silicification without the need to invoke unknown silicon biochemistry. Recent research suggests that this has now been achieved, at least for plants (Guerriero et al., 2018b). It has been demonstrated that the β-1,3 glucan, callose, is an adventitious catalyst of biogenic silica deposition in plants (Brugiére and Exley, 2017; Exley, 2015; Guerriero et al., 2018b, 2018a; Kulich et al., 2018; Law and Exley, 2011). It is a requirement of biological silicification without necessarily being the final determinant of the process. In the proposed mechanism of callose-driven biological silicification, callose and its biochemistry provide biological compartments for harvesting of silicic acid, its temporary storage as a silicic acid condensate and its subsequent delivery to environments where its deposition as biogenic silica is conducive (Fig. 3). The biochemistry of callose remains intact and unaffected by its role in biological silicification, while the advantage conferred by biogenic silica deposition may actually have acted as a positive selection pressure for callose in the evolution of plants. By using callose biochemistry, silica undergoes the same remodelling (by action of e.g. β-1,3-glucanase) and is found in all the subcellular places where the β-1,3-glucan polymer is either temporarily or stably found (contact points of pavement cells in e.g. primitive plants, radial fibrils of stomata cells, trichome bases, plasmodesmata, etc.…) (Brugiére and Exley, 2017; Exley, 2015; Guerriero et al., 2018b, 2018a; Kulich et al., 2018; Law and Exley, 2011; Sotiriou et al., 2018). The wide variety of shapes of silicified plant cells can be explained by taking into account the role of vesicles (travelling along the microtubular network) in trapping silicic acid and carrying it to the plasma membrane together with glycosyltransferases (GTs) involved in cell wall formation (Fig. 3). Callose synthase travelling in Golgi-derived vesicles along microtubule tracks (Verma and Hong, 2008) is therefore confined with silicic acid in the same microenvironment. The delivery of the GTs at the plasma membrane would also release silicic acid, which, subsequently is trapped into the structure of the newly synthesized callose polymer and induced to condense into silica (Fig. 3). The presence of callose in endocytic vesicles has been previously described in the literature, a finding corroborating the functional versatility of this glucan (Guerriero et al., 2018b; Xu and Mendgen, 1994).

There are cell wall matrix polysaccharides synthesized in the Golgi cisternae (pectins and hemicellulose) and transported in Golgi-derived vesicles (Driouich et al., 2012) which could therefore partake in silicic acid condensation; however, so far, there is clear evidence of a role in templating silicification, both *in planta* and in vitro, only for callose (Brugiére and Exley, 2017; Exley, 2015; Guerriero et al., 2018b, 2018a; Kulich et al., 2018; Law and Exley, 2011). Callose is probably the most plastic cell wall polymer. Its deposition during crucial plant developmental processes [pollen development, cell division, plasmodesmata formation, response to pathogen attack (Chen and Kim, 2009), as well as stomata (Apostolakos et al., 2009) and trichome differentiation (Kulich et al., 2018)], together with its physico-chemical characteristics [amorphous polymer acting as a "sponge" providing microenvironments favourable for silicic acid condensation (Exley, 2015)], make it an ideal catalyst for biological silicification and provide an explanation for the great richness of silicified plant cell shapes found in nature (Fig. 3).

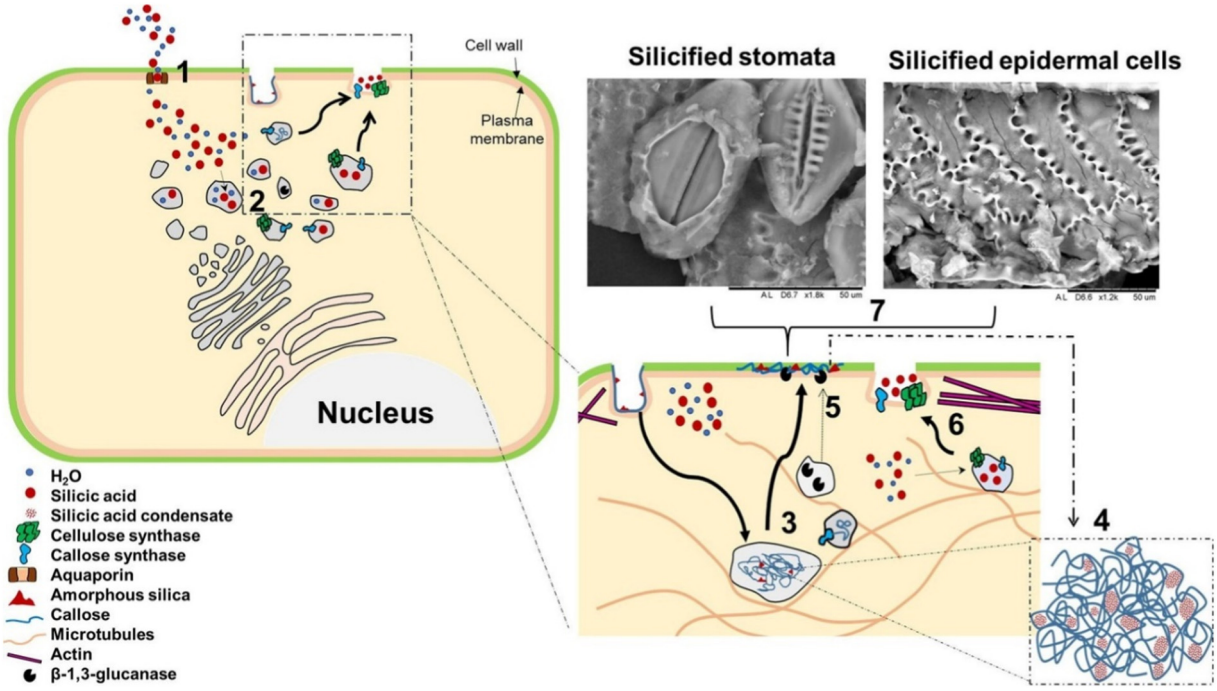

Fig. 3. Schematic depicting callose-catalysed silicification in a model plant cell. 1. Silicic acid enters via an aquaporin channel. 2–3. Adventitious capture of silicic acid by vesicles involved in callose biochemistry and callose/callose synthase transport. 4. Callose/silicic acid condensate is transported to sites where callose is used. 5. Callose/silicic acid condensate is remodelled by β-1,3-glucanases as dictated by cell morphology. 6. Entry of silicic acid in a secretory vesicle delivering cell wall-forming enzymes. 7. Examples of cells with silicified walls showing fine structural details: stomata with radial fibrils and epidermal cells with interdigitated lobes.

6. Silicic acid; a beneficent molecule

While silicon is not strictly an essential element in biota, it is beneficial in most if not all living things. For example, the green alga *Chlorella vulgaris* has no requirement for silicon to complete its life cycle successfully. However, the addition of silicic acid to culture media increases the growth rate of *Chlorella* by concomitantly increasing the biological availability of the essential nutrient phosphorus (Exley et al., 1993). The research showed that the latter is achieved because aluminium, a ubiquitous contaminant of most environments, binds phosphate and so limits its biological availability. However, in the presence of silicic acid, hydroxyaluminosilicates formed preferentially to aluminium hydroxyphosphates and thereby made phosphate more available to the alga, stimulating faster growth.

Life in the Aluminium Age and consequent burgeoning human exposure to aluminium may already be impacting negatively on human health. While silicon is not an essential element in humans, myriad examples suggest health benefits, perhaps first postulated by Pasteur in the mid-nineteenth century (Dobrzyński and Exley, 2010; Exley, 2012). Relatively recent research demonstrates that silicic acid helps to lower the body burden of aluminium, primarily by facilitating its excretion from the body (Davenward et al., 2013; Jones et al., 2017). The health benefits of silicic acid in humans, like *Chlorella*, emanate from its antagonism of aluminium toxicity. Some organisms, the biosilicifiers, such as diatoms, Radiolarians, sponges and many plants additionally benefit from silicic acid in that they deposit it as biogenic silica in their tissues. The adventitious deposition of silica offers myriad advantages to these organisms, and there is evidence, certainly historical, that similar benefits accrue from silica deposition in tissues in humans (Nielsen, 2014).

The simplicity of silicic acid totally belies its essential role in the evolution of life on Earth, in the beginning, the present and the future. Its primordial presence dictated the nature of the biochemistry of early life (Exley, 2009a), and hence thereafter, the diversity of biota up to this day. As a proposed environmental thermostat, it optimised conditions, on water, land, and in the air, under which life flourished. In the future, how will silicic acid's natural control of living processes be circumvented by human activity? Climate change and the Aluminium Age are very recent human attributions that are occurring concomitantly with natural fluctuations in the global silicon cycle leading to lower levels of silicic acid across Earth's surfaces (Exley, 1998). Now is not the time to be complacent about silicic acid, the omniscient benefactor.

Conflict of interests statement

The authors have no conflict of interests to declare.

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